Separation of ternary mixtures by extractive distillation with 1,2-ethandiol and glycerol

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ABSTRACT

Continuous extractive distillation is a widely used method to separate binary and multi-component azeotropic mixtures. Large-scale application and heavy energy usage play an important role in discovering more efficient separating agents. Separating agent (entrainer) selection for extractive distillation of binary mixtures is usually based on the analysis of relative volatility diagrams of components to be separated. Selective effect of entrainer is due to the differences in character and intensity of intermolecular interactions between entrainer and original mixture compounds. Accordingly, it is reasonable to additionally evaluate excess Gibbs energy magnitudes in binary systems formed by compounds of original mixture and entrainer (Raeva et al., 2011a).

Separating agent selection based on thermodynamic criterion is not uniquely defined for ternary mixtures yet. It establishes some steps of entrainer choice for extractive distillation of ternary mixtures containing several azeotropes. Substantiation of entrainer efficiency is proved by separation of industrial mixtures: tetrahydrofuran–methanol–water, ethyl acetate–ethanol–water and acetonitrile–methanol–water.

1,2-Ethandiol is well known to be an effective entrainer for different type of systems, including aqueous mixtures of organic substances (Gomez and Gil, 2009; Frolkova and Raeva, 2010). Glycerol is becoming more embroiled into separation processes due to environmental issues. They both fill in the common requirements for entrainer: by sufficiently changing the relative volatility of the substances to be separated and avoiding formation of new azeotropes with components of separating mixtures.

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1. Introduction

One of the main concerns, related to major health and environmental issues in the chemical, pharmaceutical and special industry, is solvent waste (Kim and Smith, 2004; Jimenez-Gonzalez et al., 2005), which frequently contains different compounds, e.g. alcohols, ethers, esters, and water.

Separation of such mixtures is complicated by azeotrope phenomenon, which makes conventional processes based on vapor–liquid equilibria (VLE) not feasible. Although interesting membrane techniques not governed by VLE are investigated in literature (Brüschke and Tusel, 1986), they do not allow for separation of large amounts of solvents, and currently present additional technological features which cause regeneration difficulties. Also, in recent years, ionic liquids (Han and Row, 2010; Marciniak, 2010; Lei et al., 2014) have been introduced in the separation field, which, due to their remarkable properties, can be considered as very effective non-volatile entrainers, but in large scale chemistry are not yet widely applied, mostly due to financial and economic reasons. However, it is shown that in some cases high boiling entrainers are of more efficiency than ionic liquids (Navarrete-Contrerasa et al., 2014)
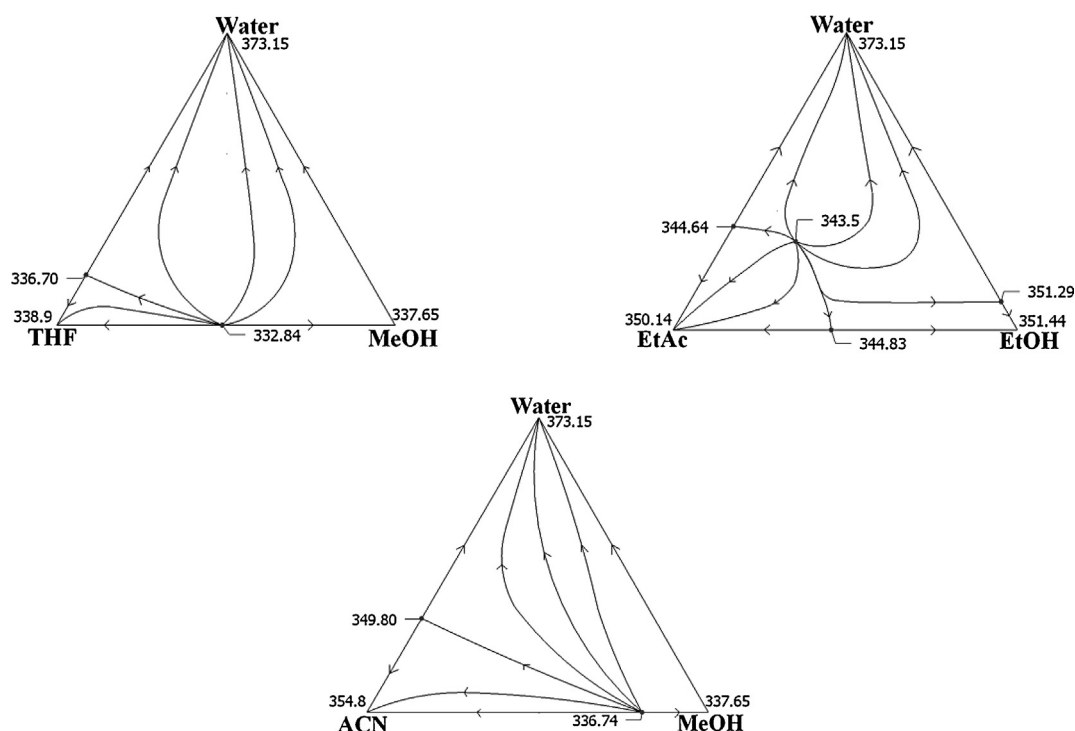

Fig. 1 – Residue curve map plot at 101.3 kPa for ternary systems. (Aspen One 7.3), THF–tetrahydrofuran, MeOH–methanol, EtAc–ethyl acetate, EtOH–ethanol, ACN–acetonitrile.

Another interesting solution based on VLE, is represented by extractive distillation process. The process implements adding entrainer, which, combined into the interactions with components of original mixture, selectively changes relative volatility of separated compounds. Correctly chosen entrainer helps to minimize energy consumptions and negative environmental impact on separation processes (Gomez and Gil, 2009).

In this paper we investigate and discuss the separation aspects of three ternary industrial systems, namely tetrahydrofuran–methanol–water, ethyl acetate–ethanol–water and acetonitrile–methanol–water at 101.3 kPa, which contain more than one azeotrope and correspond to diagrams 2.0-2b and 3.1-2 in Serafimov's classification (Kiva et al., 2003) (Fig. 1).

Though binary azeotropes compositions are sensitive to changes in pressure, pressure-swing distillation is not preferable for all compositions of ternary mixtures due to high-energy consumption.

The feasibility of ED process for separation is investigated in this paper. It is well known, that entrainer selection influences a lot on the energy consumptions, so our research work is directed to the establishing connections between physicochemical characteristics of system in entrainer presence and selective properties of entrainer, which straightforwardly influence the energy consumptions of ED column. Its application is illustrated by separation of three industrial ternary mixtures mentioned above. This approach is suggested for further application for potential entrainer efficiency evaluation when separating systems containing several azeotropes.

2. Results and discussion

2.1. Thermodynamic criterion to select entrainers

Excess Gibbs energy is a quantitative and qualitative characteristic of intermolecular interactions in binary and multicomponent solutions. To choose agents for extractive distillation of binary azeotropic mixtures, thermodynamic criterion was proposed, establishing a relationship between excess Gibbs energy (g^E) of systems i – entrainer, j – entrainer (i, j – azeotrope forming components) and the relative volatility of substances to be separated. Entrainer efficiency is evident when difference in values Δg^E for systems i – entainer and j – entrainer is approximately equal to or higher than 1000 J/mol (Raeva et al., 2011a).

Validation and application of thermodynamic criterion was suggested and checked elsewhere (Raeva et al., 2011a,b, 2013; Sazonova et al., 2013a,b, 2014; Raeva and Sazonva, 2014). Table 1 represents major binary systems of different types and entrainers, which have been previously chosen on its basis.

In this paper entrainer selection on the basis of excess Gibbs energy analysis for separation of ternary mixtures, containing more than one azeotrope is proposed. Potential entrainer should influence symbatically the relative volatility of the same azeotrope forming component, which will provide the possibility to use only that entrainer during the whole process. In the discussed systems entrainer should increase volatility of THF, ACN and EtAc in relation to other components.

Maximum difference in Δg^E between THF–EG and methanol–EG is equal to 1100 J/mol, THF–EG and water–EG exceeds 1200 J/mol (Fig. 2). Corresponding values for EtAc–EG and ethanol–EG, EtAc–EG and water–EG reach 800 and 1700 J/mol. Excess Gibbs energy difference for ACN–glycerol and methanol–glycerol is about 1500 J/mol and for ACN–glycerol and water–glycerol exceeds 2000 J/mol.

As one may see above, criterion values for 1,2-ethandiol (EG) in systems tetrahydrofuran–methanol–water and ethyl acetate–ethanol water and criterion for glycerol in system acetonitrile–methanol–water are sufficient for all binary azeotropic mixtures of systems